PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
B32B 15/02, B01D 39/20, B22F 7/00, B32B 5/26

A1

(11) International Publication Number: WO 94/14608

(43) International Publication Date: 7 July 1994 (07.07.94)

(21) International Application Number: PCT/BE93/00079

(22) International Filing Date: 9 December 1993 (09.12.93)

(30) Priority Data:
9201110 18 December 1992 (18.12.92) BE

(71) Applicant *(for all designated States except US)*: N.V. BEKAERT S.A. [BE/BE]; Bekaertstraat 2, B-8550 Zwevegem (BE).

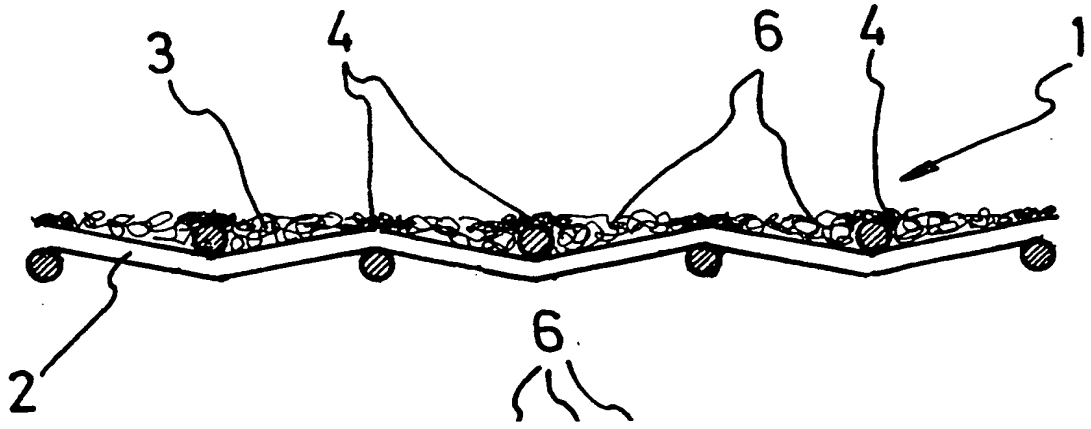
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: SAELENS, Johan [BE/BE]; Runenstraat 11, B-8800 Roeselare (BE). DE BRUYNE, Roger [BE/BE]; Paradijsstraat 9, B-9870 Zulte (BE). LOSFELD, Ronny [BE/BE]; Kuiperstraat 41, B-8790 Waregem (BE).

(74) Agent: RYCKEBOER, Leo; N.V. Bekaert S.A., Bekaertstraat 2, B-8550 Zwevegem (BE).

(81) Designated States: AU, CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: POROUS SINTERED LAMINATE CONTAINING METAL FIBERS



(57) Abstract

The invention relates to a porous laminate (1) comprising a metal wire mesh (2) of mutually crossing wires to which is bonded a non-woven web (3) of metal fibers (5) sintered to one another under pressure, in which the porosity of the membrane in the region of the junctions (4) of the mesh is at most 40 % of the porosity in the central zones (6) of the mesh openings between said junctions, along with a method for fabricating this laminate.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

POROUS SINTERED LAMINATE CONTAINING METAL FIBERS

The invention relates to a porous sintered laminate comprising a mesh of metal wires to which a non-woven web of metal fibers is bonded by a sintering operation. It relates also to a method for manufacturing this laminate.

Porous sintered metal fiber laminates reinforced with one or more metal wire meshes are generally known. U.S. patent 3,437,457, for example, relates to a layered porous structure in which a metal fiber web is bonded by sintering on at least one of its flat sides to a woven wire mesh. To accomplish this, the metal fiber web is pressed against the wire mesh under low pressure and heated so that diffusion bonds are formed in the mutual contact points of the fibers with one another and with the net. A sintered filter structure with homogenous porosity is known from German patent application 2,720,278. To produce it, woven and/or non-woven layers of thin stainless steel fibers possessing a polygonal cross-section are laid on top of one another and then sintered to one another by the simultaneous application of pressure and heat in an oven. These porous laminates are intended especially for use as depth filters, and therefore the percentage content of fibers in them is quite high. U.S. patent no. 4,126,560 can also be referred to as an example of the current state of the art.

It is an object of the invention to provide porous laminates that have a relatively low porosity combined with a satisfactory filtering capacity. In particular, the invention can provide such porous laminates in which the percentage content of fiber is relatively small compared to the space occupied by the metal wire mesh and whereby yet a sufficient filtering capacity is maintained. In this case this means that despite a relatively low fiber weight per m^2, sufficiently low porosities and suitable air permeabilities can nevertheless be achieved,

particularly in the filter surface zones facing the wire mesh openings.

Another object of the invention is to provide filter laminates containing metal fiber, and relatively thin filter laminates in particular, which are capable of resisting high pressure drops and especially pressure pulses.

It is also the intention to provide filter laminates in which the bonding between fibers and wire mesh is so strong that the fiber layers can in fact no longer be pulled apart from the mesh.

Next, and in contrast to the continuous sintering process in ovens according to the state of the art, it is an object of the invention to provide a specific continuous sintering process that does not require the use of an oven. In particular, with this specific continuous sintering method it is an object of the invention to provide a universal, economical and flexible manufacturing method, which in principle makes it possible to utilize simpler and less expensive sintering installations. More in particular, this new continuous method should enable the realization of new specific filter structures with special filtering characteristics, including the laminates containing metal fibers which are intended by the present invention.

According to the present invention, these objectives are fulfilled by a porous laminate comprising a metal wire mesh consisting of mutually crossing wires upon which a non-woven web of metal fibers sintered to one another under pressure is attached, in which the porosity of the web in the region of the mesh junction points is at most 40 % - and preferably not more than 25 % - of that in the central zones of the mesh openings between the aforementioned junction points. For particular applications, a porosity ratio of even lower than 15 % can be selected.

The economical method of producing the porous laminate envisaged by the invention works as follows: a metal wire mesh together with a metal fiber web laid on top of it is advanced continuously between rotating pressure rollers which are charged with different electrical potentials such that an electrical current flows through the cross-section of the laminate in the zone of contact with the rollers in view of sintering the fibers to one another at their points of mutual contact and to the mesh.

All this will now be explained in connection with particular embodiments of the invention with reference to the accompanying drawings. Additional characteristics and advantages will also be clarified.

Figure 1 relates to a cross-section of a porous laminate according to the invention.

Figure 2 shows a view from above of the laminate according to figure 1.

Figure 3 is an enlargement of the cross-section according to figure 1.

Figure 4 is an enlargement of a cross-section of a porous laminate according to the state of the art.

Figure 5 shows an enlargement of the appearance of the surface of the fibers in the web, which is part of a laminate according to the invention.

Figure 6 shows an analogous appearance of the fibers in a porous laminate according to the state of the art.

Figure 7 represents schematically in cross-section an apparatus for the continuous production of a porous laminate according to the invention.

The porous laminate 1 sketched in Figure 1, comprises a woven metal wire mesh 2 consisting of warp and weft wires crossing one another, to which a non-woven web 3 is bonded by sintering. The wires of the mesh are, for example, stainless steel wires

obtained by means of wire drawing. The web 3 consists of metal fibers composed, for example, of stainless steel fibers 5 which have been obtained, for example, by means of bundled drawing or by a cutting or machining operation. As is known, these fibers normally have an irregular surface with a number of sharply outlined irregularities 10, grooves and sharp edges resulting from a polygonal cross-section, etc. The use of these fibers 5 and the dry method of web formation is known in itself, for example, from U.S. patents 3,469,297 or 3,505,038. The fibers have a cross-sectional surface area of between 3×10^{-6} mm^2 and 1.8×10^{2} mm^2, and preferably between 1.2×10^{-5} and 3×10^{-3} mm^2, and even more preferably between 5×10^{-5} and 7.5×10^{-4} mm^2.

The new and specific consolidation operation of wire mesh 2 with web 3 comprises a sintering operation under high pressure which is described below. According to the invention, this results in a laminated structure with strongly compressed zones in the region of the mesh junction points 4 of the net as illustrated in Figure 2. Between these compressed zones 4, particularly in the region or area of the centers 6 of the mesh openings, more porous zones are present. This characteristic is also visible in the cross-section sketch in Figure 3. This sketch, moreover, clearly illustrates the irregular cross-section of the fibers 5. As a consequence of the strong compression of the laminate during sintering the mesh wires normally acquire a flattened zone 8, at least in the zone of the junctions 4, among other places on the outer side facing away from the web 3. The compacted fibers also display a somewhat flattened cross-section in this zone.

The sintering process according to the invention does not bring about any significant recrystallization in the steel wire mesh or in the fibers. The linearly oriented metallographic structure 7, a result of the wire drawing, is largely conserved after sintering, (see Figure 3). This contrasts with a classi-

cal sintering process, in which a significant recrystallization does occur, as is represented in Figure 4. With a classical process the web compression in the region of the mesh junctions 4 is also much less pronounced or even absent. After sintering according to the invention the fibers largely retain their rough, uneven surface with sharply outlined irregularities or striations 10, as sketched in Figure 5. With a classical sintering process, however, many of these original surface grooves or ribs disappear, which results in a surface possessing a kind of bamboo structure 9, as shown in Figure 6. Figure 5 also shows that the fibers become more firmly entangled and anchored in one another as a result of the high pressure at the mutual crossing points. The further consolidation resulting from the sintering has the consequence, then, that the fibers become bonded very strongly to one another and to the mesh, so that it becomes virtually impossible for them to tear loose.

The continuous manufacture of the porous laminate according to the invention works as follows. A relatively highly porous metal fiber web 11 is laid down over a metal wire mesh 2 and, after an optional light pre-compression treatment using a roller 12, this layered structure is fed continuously over a feed table 13 through the actual consolidation device (Figure 7). This device comprises essentially a system of metal pressure rollers 14 and 15, between which a difference of potential is set from an electrical source "E" such that an electrical current will flow over the cross-section of the laminate in the narrow, strip-shaped zone of contact 16 with the rollers, which section lies perpendicular to the direction of movement of the laminate.

The difference of electrical potential can, if so desired, be regulated according to the nature and characteristics of the laminate. In fact, the electrical current, whether DC or AC, has the effect of a resistor heating process, which results in the fibers being sintered together at their contact points.

However, since the contact time is relatively short, very high pressures are required. These high pressures then result in a high degree of compression and a local flattening, a pressing into one another or constriction of the fibers and mesh wires in the region of the junctions 4 (see Figure 5). One consequence, then, is that there is often a local flattening 8 of the wires 2 on their exterior sides. In practice it is virtually impossible to realize the same sintering bonding characteristics with a classical sintering process in an oven since the pressure forces applied there over great surface areas would have to be much too high. It would also be impossible to achieve the same sintering bonding characteristics and the low porosities by means of the cold rolling that is usually done to compress the sintered porous fiber structures after a classical sintering treatment, whether in a discontinuous or a continuous process. The cold rolling pressure would have to be so high that the porous web structure would be crushed in the region of the mesh junctions.

Example

A number of non-woven webs having weights of either 300 g/m^2 or 600 g/m^2 and made of stainless steel fibers of the 316L type, which is obtained by bundled drawing, were combined according to the invention with various woven wire gauzes, each having a thickness of 0.5 mm (i.e. with wire diameters of 0.25 mm). The mesh sizes of the gauzes or nets in this case differed as indicated in the table below. Various equivalent fiber diameters of resp. 8, 12 and 22 microns were also utilized.

The laminates were fed into an apparatus as shown in Figure 7 between two pressure rollers 14 and 15, at a suitable speed, for example, of between 0.1 and 5 m/min. The pressure exerted on the laminate passing between the rollers was of the order of between 10 and 30 N/mm^2 and the tension applied resulted in a current through the cross-section of the laminate running up to 25,000 A for a laminate breadth of 40 mm. The apparatus was

equipped with a current control device to avoid current picks or short circuiting.

The table below gives the average air permeability values (AP) recorded at a pressure gradient of 200 Pa. In each case the test section had a surface area of 0.62 cm^2. By way of comparison, in test no. 13 an analogous laminate construction was tested which had been sintered in a customary way (discontinuously) in a vacuum oven. (See also Figure 4.) This laminate was therefore considerably thicker - 0.82 mm - which resulted in the air permeability being nearly four times as great as compared with test no. 3. The pore size (MFP - mean flow pore size) is also given.

It was also found that it is impossible to pull or tear the web loose from the wire mesh in the laminates according to the invention, whereas this was possible with the classical laminate as in test 13.

TABLE

TEST NO.	FIBER Ø (µm)	WEB WEIGHT	WIRE MESH OPENING (mm)	AP l/dm².min at 200 Pa X	MFP µm X	THICK-NESS (mm)
1	22	600	0.4	264	23	0.63
2	22	300	0.4	707	35	0.44
3	12	600	0.4	111	15	0.52
4	12	600	0.45	112	15	0.49
5	12	600	0.63	141	17	0.47
6	12	600	1.25	178	22	0.45
7	12	300	0.4	360	23	0.44
8	12	300	0.45	359	24	0.44
9	12	300	0.63	497	27	0.40
10	12	300	1.25	-	-	-
11	8	600	0.4	46	10	0.57
12	8	300	0.4	159	16	0.47
13	12	600	0.4	435	30	0.82

It is easy to deduce from this table that for the same mesh opening and the same web weight the air permeability rises considerably with the increasing fiber diameter. On the other hand, with the same mesh opening and an increasing web weight, the air permeability will naturally decrease. In absolute value the decrease will be greater for thicker fibers than for thinner ones. Finally, at constant web weight and fiber diameter there is a decrease in air permeability as the mesh size decreases. The influence of the mesh size is relatively less important, however, than a change in web weight or fiber diameter.

Moreover, it is possible to deduce from test no. 10 that with a low web weight and at the same time a relatively large mesh opening the fibers probably form insufficient numbers of bridges between one another and between neighbouring mesh junctions to provide reproducible filtering characteristics.

In stead of fibers obtained by means of bundled drawing, steel wool or other metal fibers obtained by shaving or cutting (as described e.g. in EP 319.959) can be utilized and, after being processed into non-woven webs, they can be combined with appropriate mesh structures. Such fibers and webs thus obtained have been described, for example, in U.S. patent 3,505,038. Metal fibers that have been obtained directly from the meltage (molten metal) can also be utilized (such as are known from U.S. patent 3,845,805 or G.B. patent 1,455,705) or that have been obtained by means of reducing metal oxide mixtures (U.S. patent 3,671,228 and U.S. patent 4,312,670). The web formation can also be carried out by means of a wet method, as is known from or analogous to U.S. patent 3,127,668.

A knitted structure can, if so desired, also be utilized as wire mesh. The cross-section of the mesh wires need not necessarily be round: it can also be rectangular, for example. In certain cases the metal fiber web can also be sandwiched as a

central filtering layer between two wire meshes which are sintered on both sides of the webs. The wire mesh on one side of the web can then consist of thinner wires (e.g. wire diameter of 0.1 mm) than that on the other side (diameter 0.2 mm). In addition, more fiber web layers can be sintered on top of one another with a wire mesh, with the fiber diameter, for example, differing from one layer to another. The web weight can vary between 100 g/m^2 and 4 kg/m^2. If so desired, knitted or woven nets with small meshes can be stacked crosswise on top of one another and sintered to one another using the method accor-ding to the invention.

The metal fiber alloy utilized need not be limited to the various stainless steels. The use of nickel, Inconel® and Hastelloy® fibers, as well as corrosion, abrasion and/or high-temperature resistant metal fibers (e.g made of FeCrAlloy® alloys) may also be considered.

The laminate according to the invention has a very broad range of applications or uses, e.g. as filter medium. In the first instance, utilizing them as filters for air bags is considered, which bags are currently being installed in the steering columns or dashboards of some cars and that serve as cushions between passengers and the steering wheel or dashboard in case of a head-on collision. Currently, sintered metal web filters are often incorporated in these air bags for filtering the suddenly expanding gas that is released to rapidly blow up the bag when an impact shock is detected. These fiber filters must naturally be very resistant to pressure waves and shocks. The tight filter structure according to the invention is extremely well-suited to this.

In general, it is also possible to adapt the characteristics of the relatively thin filter structures of fairly low porosity in order to utilize them as surface filters. Sol-gel suspensions (e.g. ZrO_2) can also be deposited on them, or diamond like

coatings, so they can be used as inorganic membrane filters in micro or ultrafiltration, whether with tangential (cross flow) or crossways ("dead end") flow.

If high temperature resistant fibers - such as FeCrAlloy fibers - are utilized, the sintered laminates according to the invention can also be used as a flat or tube-shaped membrane for surface radiation burners or as recyclable filter for soot particles from diesel exhaust gases, for example.

Either before or after sintering the fibers can be coated, for example, with catalytically active substances so that the laminate can then be utilized as a catalyst. Coatings on the fibers consisting of oxidative catalyzers are good candidates for removing soot particles easily and at low temperatures which soot particles can be caught or arrested in diesel exhaust filters. Laminates according to the invention, comprising nickel or nickel alloy fibers, can also be utilized as electrodes.

Custom filter systems according to the invention can be designed in which a combination of one or more laminates according to the invention are installed in flat form or in tube form, whether or not combined with other filter media.

CLAIMS

1. A porous laminate (1) comprising a non-woven web (3) of metal fibers (5) sintered to one another under pressure and bonded to a metal wire mesh (2) of mutually crossing wires, wherein the porosity of the membrane in the region of the junctions (4) of the mesh is at most 40 % of the porosity in the central zones (6) of the mesh openings between these junctions.

2. A porous laminate according to claim 1, wherein said porosity is at most 25 %.

3. A porous laminate according to claim 2, wherein said porosity ratio is less than 15 %.

4. A laminate according to claim 1, wherein the fibers (5) have an uneven surface with sharply outlined irregularities or striations (10).

5. A laminate according to claim 1, wherein the fibers (5) have a somewhat flattened cross-section in the region of the junctions (4).

6. A laminate according to claim 1, wherein the fibers have a cross-sectional surface area of between 3×10^{-6} mm^2 and 1.8×10^{-2} mm^2.

7. A laminate according to claim 6, wherein said surface area is between 1.2×10^{-5} and 3×10^{-3} mm^2.

8. A laminate according to claim 7, wherein said surface area is between 5×10^{-5} and 7.5×10^{-4} mm^2 .

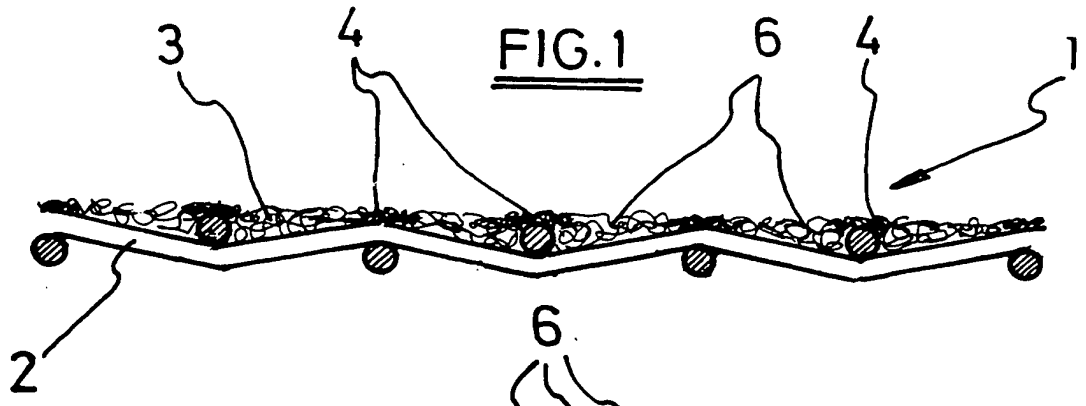
9. A laminate according to claim 1, wherein the mesh wires in the region of the junctions (4) have a flattened zone (8) on the outer side facing away from the web.

10. A laminate according to claim 1, wherein the wires of the mesh (2) display a non-recrystallized structure.

11. The use of the laminate according to claim 1 as a filter medium.

12. A method for manufacturing a porous laminate according to claim 1, wherein a metal wire mesh (2), together with a metal fiber web (11) laid on top of it, are continuously advanced between rotating pressure rollers (14, 15) ; these rollers have differing electrical potentials such that an electrical current is transmitted through the cross-section of the laminate in the zone of contact (16) with the rollers to sinter the fibers (5) together at their mutual points of contact and to the mesh (2).

FIG.1



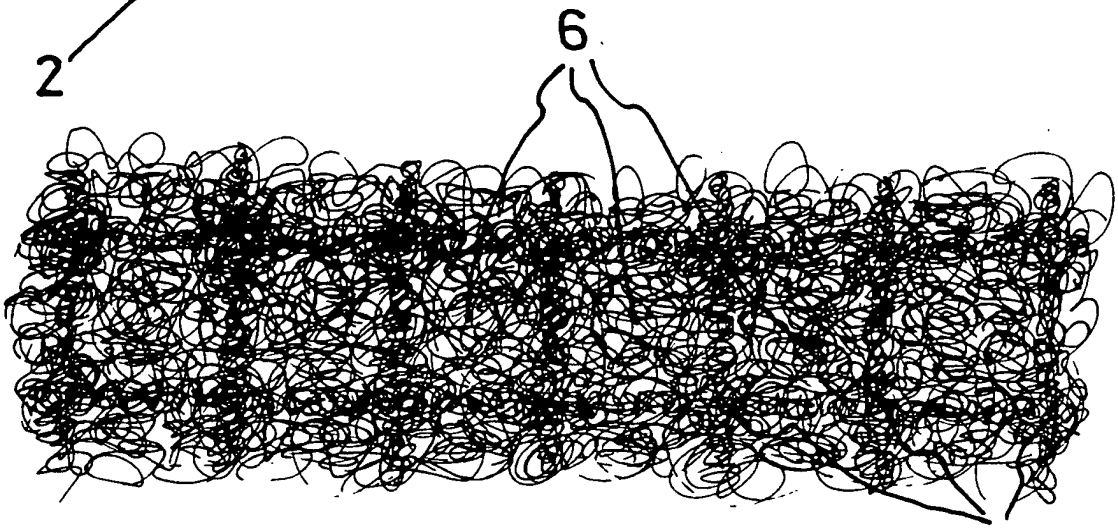


FIG.2

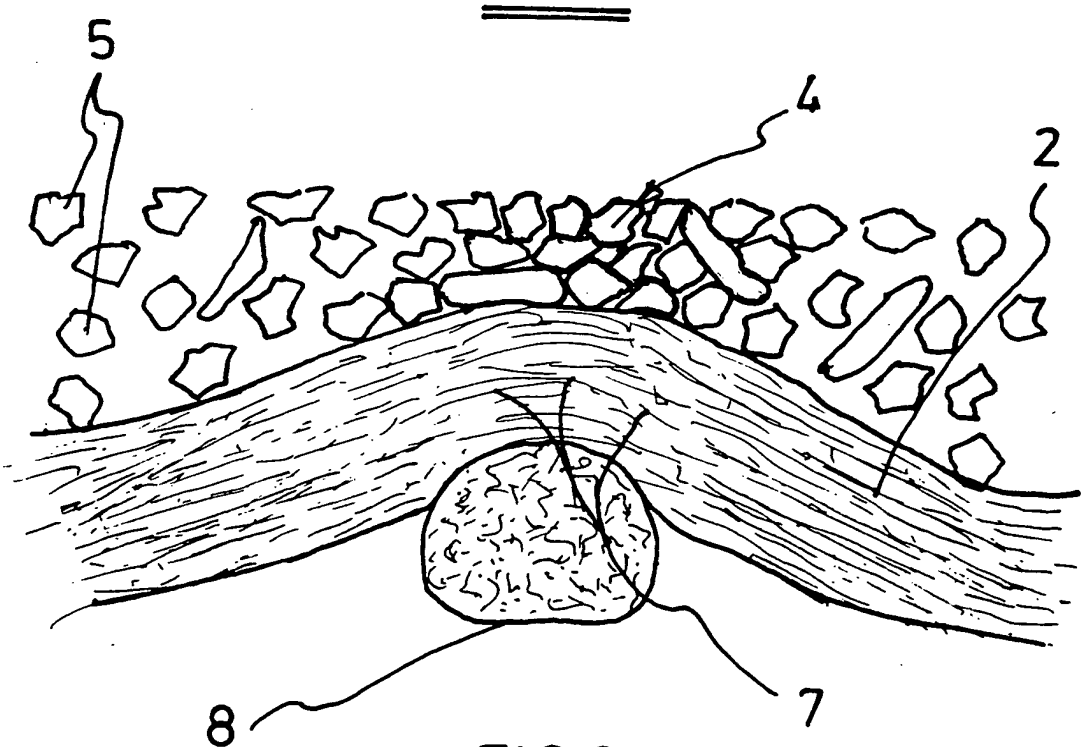


FIG.3

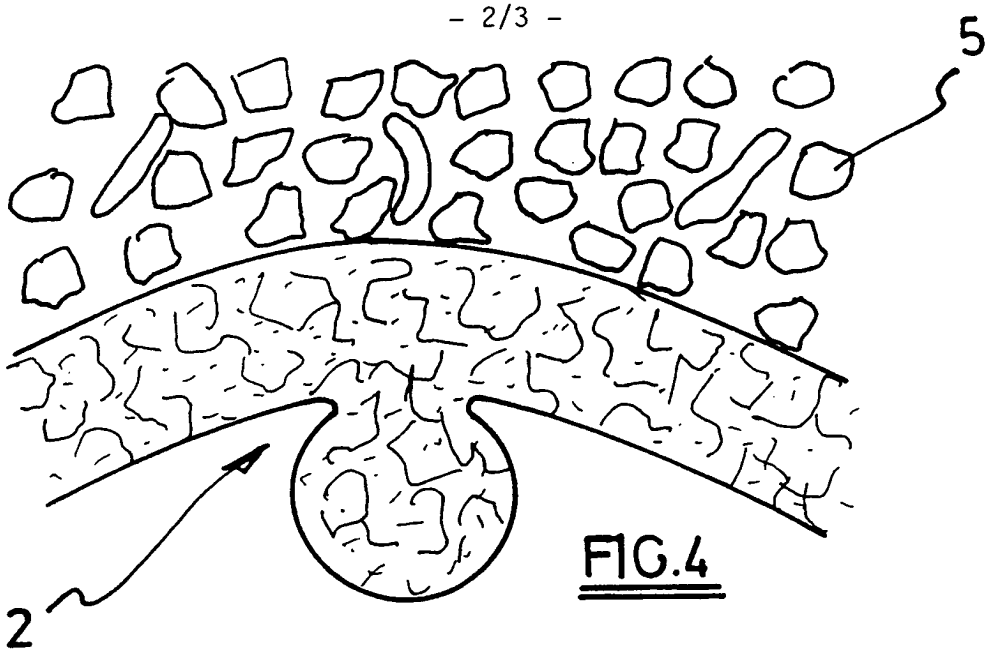


FIG.4

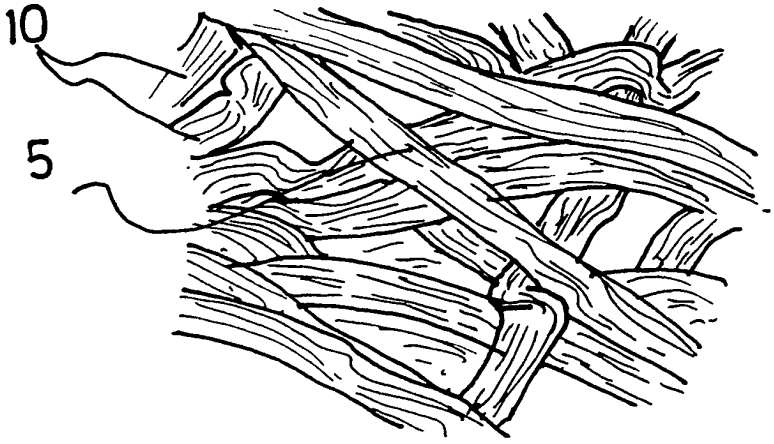


FIG.5

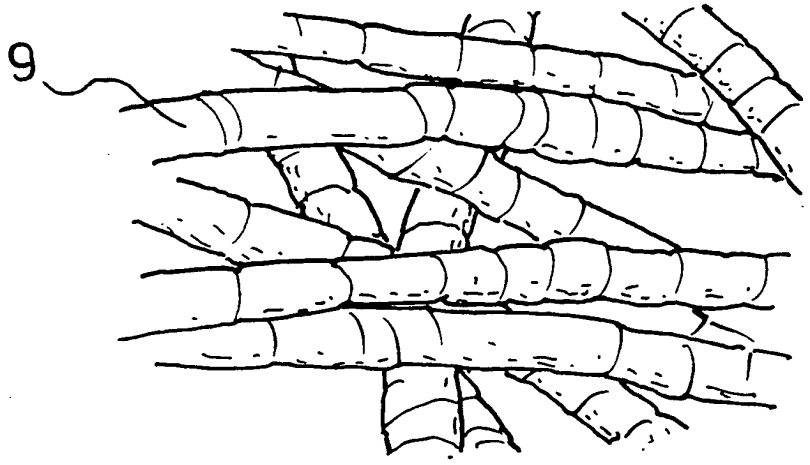


FIG.6

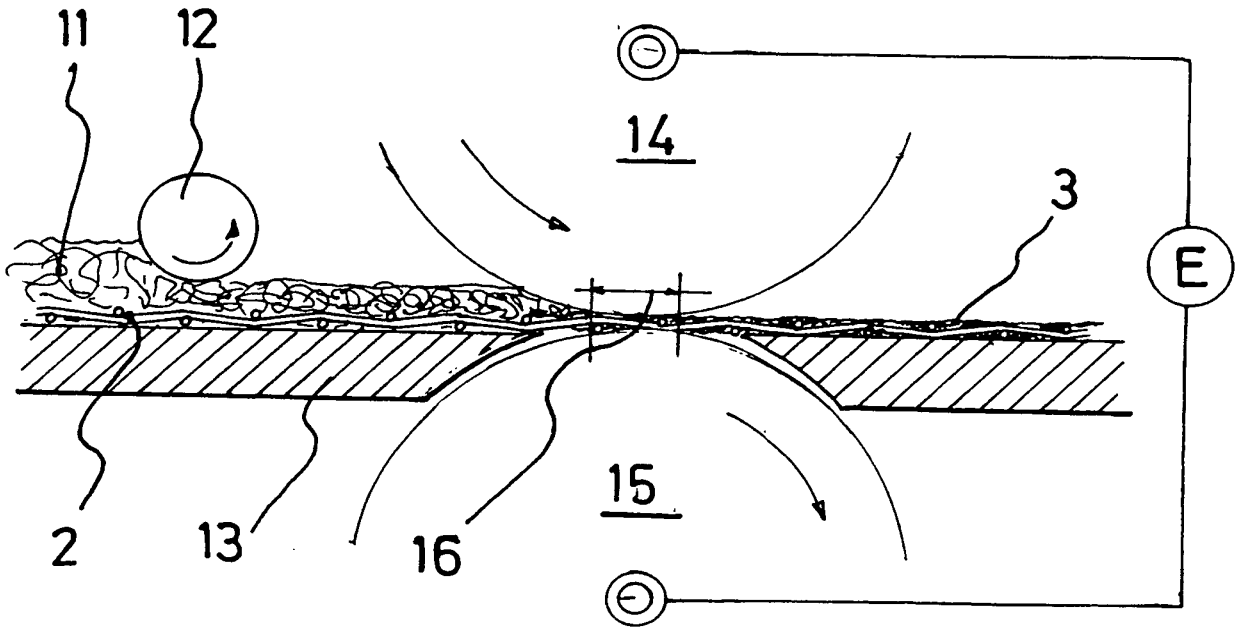


FIG. 7

INTERNATIONAL SEARCH REPORT

[redacted]tional Application No
[redacted]/BE 93/00079

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B32B15/02 B01D39/20 B22F7/00 B32B5/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 B32B B01D B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,27 20 278 (NIPPON SEISEN CO. LTD.) 9 November 1978 cited in the application see page 6, line 6 - line 22 see page 9, line 16 - line 26 see page 10, line 17 - line 24; figure 6	1,4,11
A	BE,A,890 312 (N. V. BEKAERT S.A.) 11 March 1982 see page 3, line 19 - page 4, line 9; figure 2	1
A	US,A,4 126 560 (MARCUS ET AL.) 21 November 1978 cited in the application see claim 1; figure 1	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 April 1994	19. 04. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	**Authorized officer** McConnell, C

Form PCT/ISA/210 (second sheet) (July 1992)

International Application No
PCT/BE 93/00079

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,19 24 836 (G. BOPP & CO.) 15 January 1970 see page 5, line 6 - page 6, line 11; figures	1
A	DE,A,21 47 735 (BATTELLE-INSTITUT E.V.) 29 March 1973 see claims 1,4	12
A	BE,A,828 467 (N. V. BEKAERT S.A.) 28 October 1975	

INTERNATIONAL SEARCH REPORT

[redacted] on patent family members

[redacted]tional Application No
[redacted]BE 93/00079

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-2720278	09-11-78	NONE		
BE-A-890312	11-03-82	NONE		
US-A-4126560	21-11-78	BE-A-	852823	18-07-77
		CA-A-	1094957	03-02-81
		DE-A,C	2715289	03-11-77
		FR-A,B	2348986	18-11-77
		GB-A-	1575049	17-09-80
		JP-C-	1258913	12-04-85
		JP-A-	52131262	04-11-77
		JP-B-	59033009	13-08-84
		JP-C-	1341975	14-10-86
		JP-A-	59192707	01-11-84
		JP-B-	61002407	24-01-86
		LU-A-	77191	12-08-77
		NL-A-	7704340	25-10-77
DE-A-1924836	15-01-70	CH-A-	462783	
DE-A-2147735	29-03-73	NONE		
BE-A-828467	28-10-75	DE-A-	2618700	18-11-76
		FR-A,B	2309266	26-11-76